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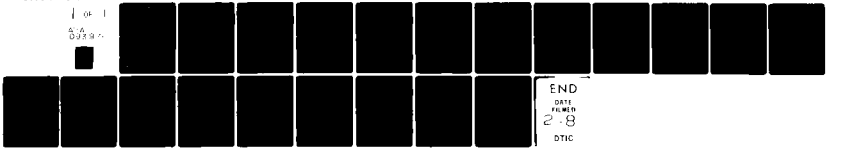

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$Fe(CO)_5$ and $Fe_3(CO)_{12}$ can be photoactivated with intense ultraviolet or visible light from a laser to yield catalytic reaction of alkenes. Irradiation for short time periods with intense light allows limits to be placed on the turnover rates for the photogenerated catalysts. Isomerization of neat 1-pentene, and reaction of neat 1/1 mole ratio $HSiEt_3$/1-pentene mixtures, at 25°C have been studies using $Fe(CO)_5$ and $Fe_3(CO)_{12}$ as the photochemical catalyst precursor. Data show that turnover rates (1-pentene molecules consumed per $Fe(CO)_5$ or $Fe_3(CO)_{12}$ molecule initially present per minute) exceed 1000 in most cases. In

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practical terms, we find that neat 1-pentene solutions can be >25% isomerized to cis- and trans-2-pentene in <5 s with ~$10^{-2}$M $Fe(CO)_5$; and 3.66 M/3.66 M, $HSiEt_3$/1-pentene can be >25% converted to non-$C_5$ alkene products in <10s at <$10^{-2}$M $Fe_3(CO)_{12}$. These data establish the photogenerated catalysts from $Fe(CO)_5$ and $Fe_3(CO)_{12}$ to be among those having the gastest turnover rates known for homogeneous organometallic catalysts. Conventional Xenon flash photolysis experiments (<100 μsec flash) indicate that catalytic action is over within seconds after the light pulse. In such experiments, a single flash can yield up to 50% conversion of neat 1-pentene to products. Intense irradiation does not significantly alter the distribution of products observed compared to previous studies employing low light intensity excitation.

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(6)

# PHOTOGENERATION OF VERY ACTIVE HOMOGENEOUS CATALYSTS USING LASER LIGHT EXCITATION OF IRON CARBONYL PRECURSORS.

by

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December 29, 1980

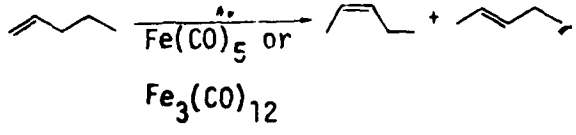
Photogeneration of Very Active Homogeneous Catalysts Using Laser Light Excitation of Iron Carbonyl Precursors

Abstract: $Fe(CO)_5$ and $Fe_3(CO)_{12}$ can be photoactivated with intense ultraviolet or visible light from a laser to yield catalytic reaction of alkenes. Irradiation for short time periods with intense light allows limits to be placed on the turnover rates for the photogenerated catalysts. Isomerization of neat 1-pentene, and reaction of neat 1/1 mole ratio $HSiEt_3$/1-pentene mixtures, at 25° C have been studied using $Fe(CO)_5$ and $Fe_3(CO)_{12}$ as the photochemical catalyst precursor. Data show that turnover rates(1-pentene molecules consumed per $Fe(CO)_5$ or $Fe_3(CO)_{12}$ molecule initially present per minute) exceed 1000 in most cases. In practical terms, we find that neat 1-pentene solutions can be >25% isomerized to cis- and trans-2-pentene in <5 s with ~$10^{-2}$ M $Fe(CO)_5$; and 3.66 M/3.66M, $HSiEt_3$/1-pentene can be >25% converted to non-$C_5$ alkene products in <10s at <$10^{-2}$ M $Fe_3(CO)_{12}$. These data establish the photogenerated catalysts from $Fe(CO)_5$ and $Fe_3(CO)_{12}$ to be among those having the fastest turnover rates known for homogeneous organometallic catalysts. Conventional Xenon flash photolysis experiments (<100 μsec flash) indicate that catalytic action is over within seconds after the light pulse. In such experiments, a single flash can yield up to 50% conversion of neat 1-pentene to products. Intense irradiation does not significantly alter the distribution of products observed compared to previous studies employing low light intensity excitation.

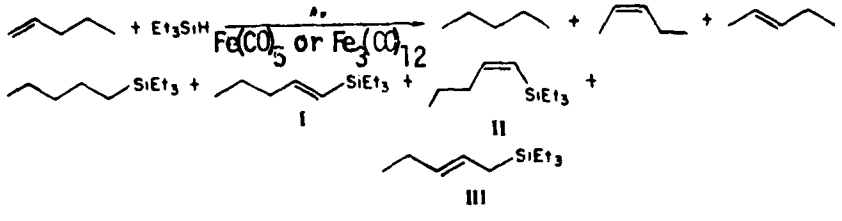
Photogeneration of Very Active Homogeneous Catalysts Using Laser Light Excitation of Iron Carbonyl Precursors

Sir:

Photoinitiation of homogeneous catalysis by irradiation of thermally inert iron carbonyl catalyst precursors has been demonstrated to be a procedure for effecting olefin isomerization, hydrogenation, and hydrosilation reactions at low temperature[1-3] compared to thermal catalysis.[4] However, there has been very little quantitative information concerning the activity of photogenerated catalysts. In this communication we wish to report preliminary experiments that show that $Fe(CO)_5$ and $Fe_3(CO)_{12}$ are photochemical precursors to thermally active catalysts that rival the fastest homogeneous catalysts known.[5] The catalytic chemistry studied has been that represented by equations (1) and (2) and the question addressed has been:




(1)




(2)

what is the turnover rate for the photogenerated catalysts? Answering such a question is important in establishing whether photoinitiation of catalysis can provide products at a useful rate. But the answer is not straightforwardly obtained, since the actual catalyst in this system is not well-characterized. We have taken an approach that allows us to put some lower limits on the activity of the catalyst.

The observed quantum yield for consumption of 1-pentene according to (1) or (2) significantly exceeds unity[1-3] and indicates that an active catalyst is generated photochemically. But the quantum yield at a single light intensity only gives the efficiency for utilizing incident quanta. The quantum yields from $Fe(CO)_5$ or $Fe_3(CO)_{12}$ photocatalyzed reactions are not found to be infinite; catalysis does not persist in the dark after photoinitiation in these systems. Sealed reaction vessels lead to the possibility of the catalyst back reacting with photoejected CO, while purging with an inert gas to remove the CO leads to clusters that are catalytically inactive. This chemistry complicates the determination of catalyst turnover rate. Thus, the approach we have taken has been to determine the observed rate of 1-pentene consumption using very high light intensity excitation where the catalyst turnover rate, not photogeneration of the catalyst, could become the rate limiting feature. The results are given below.

Photocatalysis experiments according to equations (1) and (2) were carried out using an Ar ion laser as the excitation source to provide very high light intensity. Consumption of 1-pentene as a function of irradiation time proves to be a very fast process. Typically, we have monitored the chemistry by gas chromatography, but in these experiments we found that the reaction is so fast that we became concerned about the

finite time interval involved in opening hermetically sealed ampules to quench any residual dark catalytic activity.

Irradiation of several samples for equal time followed by analysis of each at a different time after irradiation reveals no dark after effects; that is, it would appear that when the light is turned off catalysis ceases essentially instantly. The time resolution of this sort of experiment is <30 s, the time needed to quench any catalytic activity by exposing the solutions to $O_2$ by opening the hermetically sealed ampules. We have found that neat 1-pentene solutions can be quantitatively analyzed by near-infrared absorption spectroscopy. Figure 1 shows the results of catalysis on a portion of the near infrared spectrum of 1-pentene. Independent measurement of the spectra of pure cis-2-pentene and pure trans-2-pentene in the same wavelength range shows that the spectral changes shown in Figure 1 are consistent with the chemistry represented by equation (1) where the ratio of trans-2-pentene to cis-2-pentene is roughly 3 to 1. The near-infrared spectrum of 1-pentene shows bands not present in the 2-pentenes and allows quantitative analysis of 1-pentene disappearance on a time scale much faster than gas chromatography. Comparison of a near infrared spectrophotometric analysis and gas chromatographic analysis of 1-pentene disappearance show that the near infrared is a reliable quantitative technique. Monitoring the unique near infrared absorbance of 1-pentene shows that catalysis persists for <5 s after irradiation of $Fe(CO)_5$/1-pentene mixtures is terminated. Flash photolysis followed by monitoring at 1330 nm shows that catalysis is over within a few seconds after the light is switched off (vide infra).

Table I summarizes typical data for photocatalysis experiments using high light intensity continuous laser excitation. The shortest convenient irradiation time was 5 s in such experiments and roughly 25-50% conversion of neat starting material to product could be obtained using either $Fe(CO)_5$

or $Fe_3(CO)_{12}$. In reaction of $HSiEt_3$ with 1-pentene the 2-pentenes account for only ~25% of the 1-pentene reacted; that is, 75% of the 1-pentene yields n-pentane and Si-containing material. In all cases the observed quantum yield, $\Phi$, (number of 1-pentene molecules consumed per incident photon) exceeded unity and turnover rates generally exceeded 1000. The turnover rates given are based on the concentration of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ initially present and are thus lower limits. The data shown establish the catalyst from $Fe_3(CO)_{12}$ or $Fe(CO)_5$ to be among the most active homogeneous organometallic catalysts.

Determining turnover rates accurately depends on knowing the catalyst concentration and being able to simultaneously measure the reaction rate. Flash photolysis provides a way to generate a certain catalyst concentration and catalytic chemistry could be monitored in the near infrared. We find that catalytic chemistry is easily observable using flash photolysis, and we had hoped that we could monitor the decline of the 1330 nm near infrared overtone absorption following the excitation flash of <100 μs duration. Quantitative analysis, Table I, shows that a single flash can yield a large extent conversion. The difficulty is that flash photolysis of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ in 1-pentene yields a near infrared absorbing transient with a lifetime of about one second precluding a quantitative measure of the 1330 nm absorbance. The conclusion to be drawn now is that the catalytic chemistry is over within a few seconds after the excitation flash.[6] Continued effort is being directed to the use of flash photolysis to measure turnover rates.

Intense irradiation, and especially pulsed excitation, raises the possibility of unusually active species being formed.[6] For example, the primary result of irradiating $Fe(CO)_5$ is believed to be that represented by equation (3).[7] When pulsed excitation is used the leading edge of the

$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4 + CO \qquad (3)$$

pulse may effect the process represented by equation (3) while the trailing portion may effect further CO loss as in equation (4). The $Fe(CO)_4$

$$Fe(CO)_4 \xrightarrow{h\nu} Fe(CO)_3 + CO \qquad (4)$$

is known to be photosensitive with respect to CO loss in low temperature matrices.[8] Photolysis of $Fe(CO)_5$ in the gas phase can even yield Fe atoms.[9,10] The consequences of such multiple coordinative unsaturation are not known but we note no new products nor any change in the distribution of products in the photocatalyzed reactions of alkenes represented by equations (1) and (2). We have used a pulsed Nd-Yag laser (frequency tripled to yield 355 nm pulses) excitation of $Fe(CO)_5$ with <6 nsec pulses, 20 mJ/pulse, and still find no unusual effects on catalytic product distributions. Likewise, 532 nm (<7 nsec, 40 mJ/pulse) irradiation from a frequency doubled Nd-Yag laser does not alter products from $Fe_3(CO)_{12}$ photocatalysis.

To summarize our main findings, we conclude that photolysis of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ yields an exceedingly active catalyst. The active catalyst is likely not an excited state species since the excited lifetimes of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ are too short to effect catalysis.[9] The active species is likely an unsaturated ground state species photoproduced by loss of CO from $Fe(CO)_5$ or Fe-Fe bond cleavage in $Fe_3(CO)_{12}$.[1,3] Very high turnover rates for alkene isomerization and hydrosilation have been found. Moreover, very high turnover numbers (moles of product per mole of Fe initially present) are achieved. For example, when a single flash yields ~50% conversion of neat 1-pentene using $\sim 10^{-2}$ M $Fe(CO)_5$ the turnover number exceeds 400. Subsequent flashes yield an even greater extent conversion to ultimately completely equilibrate the linear pentenes.[9] High light intensity does not appear to alter the product distribution where a number of products are possible (alkene + $HSiEt_3$). The data show that very high light intensity can be used to produce product at a high observed rate and with high quantum efficiency (>>1).

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References


1. Schroeder, M. A.; Wrighton, M.S. J. Am. Chem. Soc., 1976, 98, 551 and J. Organometal. Chem., 1977, 128, 345.

2. (a) Asinger, F.Y.; Fell, B.; Schrage, K. Chem. Ber., 1965, 98, 372, 381; (b) Asinger, F.; Fell, B.; Collin, G. ibid., 1963, 96, 716; (c) Carr, M.D.; Kane, V.V.; Whiting, M.C. Proc. Chem. Soc., London, 1964, 408.

3. Austin, R. G.; Paonessa, R. S.; Giordano, P.J.; Wrighton, M.S. Adv. Chem. Ser., 1978, 168, 189.

4. (a) Howard, J.F.; Chalk, A.J. "Organic Synthesis via Metal Carbonyls", Vol. 2, Wender, I.; Pino, P., eds., Wiley: New York, 1977, p. 680-694; (b) Frankel, E.N.; Emken, E.A.; Peters, H.M.; Davison, V.L.; Butterfield, R.O. J. Org. Chem., 1964, 29, 3292 and 3620.

5. (a) James, B. R. "Homogeneous Hydrogenation", Wiley: New York, 1973; (b) Taqui Khan, M.M.; Martell, A.E. "Homogeneous Catalysis by Metal Complexes", Vol. I and II, Academic Press: New York, 1974 and references therein.

6. For additional information concerning the nature of the catalyst and its lifetime after photogeneration see the accompanying communication, Chase, D. B.; Weigert, F.J. J. Am. Chem. Soc., 1981, 103, 0000.

7. Geoffroy, G.L.; Wrighton, M.S. "Organometallic Photochemistry", Academic Press: New York, 1979.

8. (a) Poliakoff, M. J. Chem. Soc., Dalton, 1974, 210; (b) Poliakoff, M., Turner, J.J. J. Chem. Soc., Faraday, 1974, 70, 93.

9. Callear, A.B.; Oldman, R.J. Nature, 1966, 210, 730.

10. Karny, Z.; Naaman, R.; Zare, R.N. Chem. Phys. Lett., 1978, 59, 33.

Table I. $Fe(CO)_5$ and $Fe_3(CO)_{12}$ Photocatalyzed Reactions of 1-Pentene.[a]

A. Continuous Laser Irradiation.[b]

| Catalyst Precursor (conc., M) | Irrdn. λ, nm (Power, W) | Irrdn. Time, s | Reaction | [1-pentene], M[c] | % 1-Pentene[d] consumed | Φ[e] | Turnover Rate 1-pentene/ catalyst-min[f] |
|---|---|---|---|---|---|---|---|
| $Fe(CO)_5$ ($8 \times 10^{-3}$) | 333,351,364 (2.5) | 5 | isomerization | 9.14 (neat) | 27 | 68 | 3700 |
| | | 10 | | | 35 | 44 | 2400 |
| $Fe_3(CO)_{12}$ ($5 \times 10^{-3}$) | 514.5 (1.3) | 10 | isomerization | 9.14 (neat) | 7 | 11 | 700 |
| | | 30 | | | 24 | 13 | 900 |
| $Fe(CO)_5$ ($1 \times 10^{-2}$) | 333,351,364 (2.5) | 5 | hydrosilation | 3.66 | 42 | 42 | 1700 |
| | | 10 | | | 50 | 24 | 1000 |
| $Fe_3(CO)_{12}$ ($5 \times 10^{-3}$) | 514.5 (7.5) | 10 | hydrosilation | 3.66 | 42 | 5 | 1800 |
| | | 20 | | | 59 | 3 | 1300 |

B. Flash Photolysis Excitation.[g]

| Catalyst Precursor (conc., M) | Reaction | [1-pentene], M[c] | % 1-pentene[d] consumed |
|---|---|---|---|
| $Fe(CO)_5$ ($1.4 \times 10^{-2}$) | isomerization | 9.14 (neat) | 46 |
| $Fe(CO)_5$ ($1.1 \times 10^{-2}$) | hydrosilation | 3.66 | 23 |
| $Fe_3(CO)_{12}$ ($5.1 \times 10^{-3}$) | hydrosilation | 3.66 | 25 |

[a]Reactions were generally carried out at 25°C; stirred, 1.0 ml of freeze-pump-thaw degassed solution was irradiated in hermetically sealed Pyrex ampules. Analysis for reaction was by gas chromatography or by near infrared spectrophotometry (see text). Product ratios for isomerization were determined using a 30' x 1/8" 20% Propylene Carbonate on Chromosorb P column operated at 20°C and hydrosilation products were quantitated using a 30' x 1/8" β,β'-ODPN column operated at 50°C. Control experiments show that no photoreaction occurs in the absence of $Fe(CO)_5$ or $Fe_3(CO)_{12}$; none is expected since 1-pentene and $Et_3SiH$ are transparent to light transmitted by Pyrex.

able I. (continued)

[b] The irradiation source was either a Spectra Physics Model 164 Ar ion laser or a Coherent Radiation CR18 Ar ion laser tuned to the indicated wavelength and power. The beam diameter was ~2 mm.

[c] For isomerization reactions the 1-pentene was used as solvent. For hydrosilation $HSiEt_3$ and 1-pentene were used in a 1/1 mole ratio (3.66 M/3.66 M) without any diluent but using n-hexane as an internal standard for gas chromatographic analyses.

[d] Data shown are for total amount of 1-pentene consumed. For isomerization the only products are trans- and cis-2-pentene but in the presence of $HSiEt_3$ the products also include n-pentane, (n-pentyl) $SiEt_3$, and three isomers of (pentenyl) $SiEt_3$.[1] The per cent of 1-pentene that reacts to form n-pentane and Si-containing material is ~75% under the conditions used; i.e. isomerization accounts for only ~25% of 1-pentene disappearance.

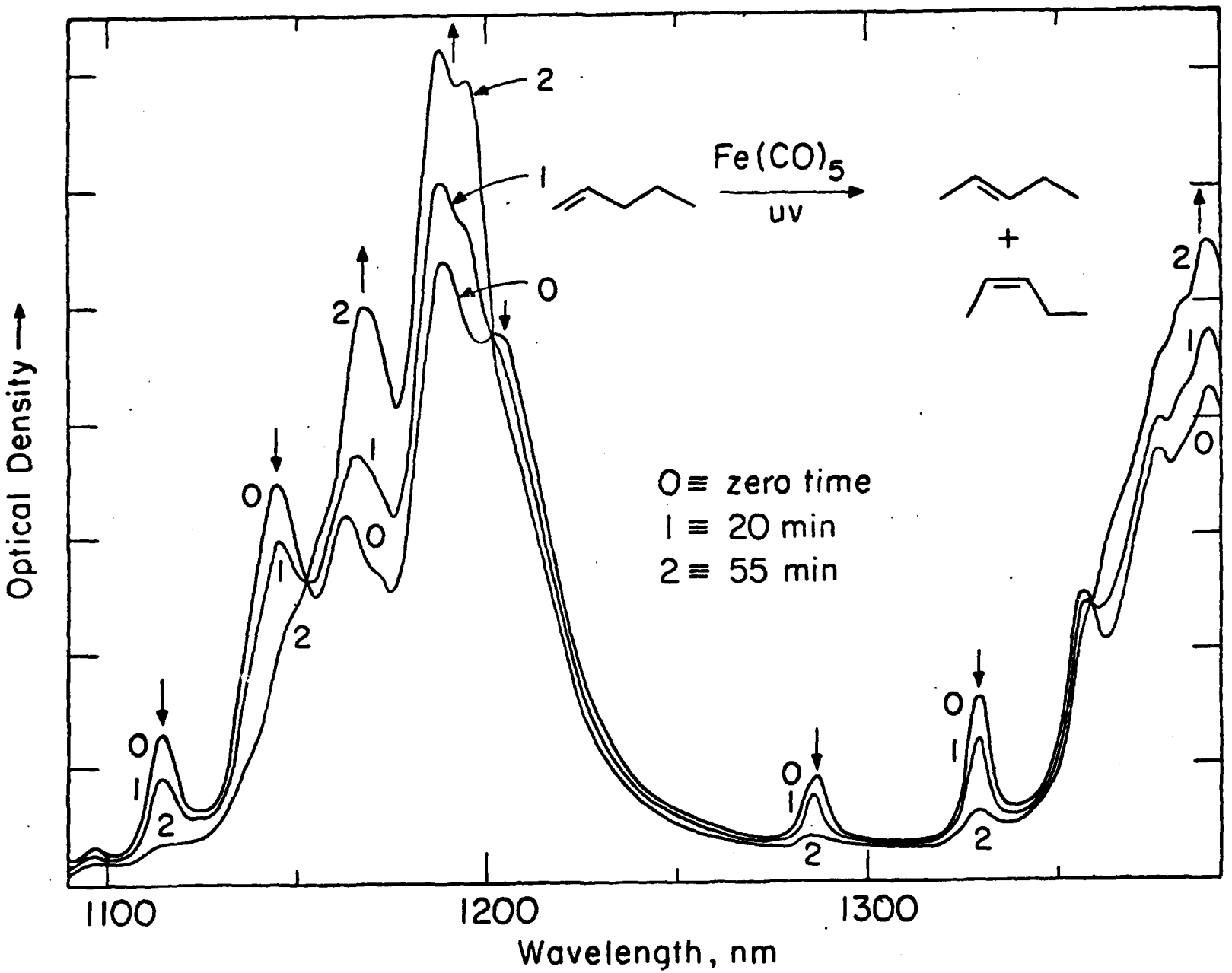
[e] Number of 1-pentene molecules consumed per photon incident on the sample.

[f] Turnover rate is given assuming all $Fe(CO)_5$ or $Fe_3(CO)_{12}$ forms a catalyst during the period indicated. Thus, these are lower limits on the turnover rate.

[g] Flash photolysis was done using a Xenon Corp. Model 710 apparatus and excitation was one 10 kV, 2000 J, <100 μsec flash of a 1.0 ml degassed sample in a Pyrex ampule.

## Figure Caption

Near infrared spectral changes accompanying ultraviolet irradiation (355 nm ± 20 nm, ~$2 \times 10^{-6}$ ein/min) of 2.0 ml of 1.86 x $10^{-2}$ M $Fe(CO)_5$ in neat 1-pentene. Features with an arrow pointing down are associated with the 1-pentene that is consumed; features with an arrow pointing up are associated with the cis- and trans-2-pentene products formed in a ~1:2.8 ratio.


Optical Density
Wavelength, nm
1100
1200
1300
Fe(CO)5
uv
+
0 ≡ zero time
1 ≡ 20 min
2 ≡ 55 min

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